GUIDE TO INTERMEDIATE BAND SOLAR CELL RESEARCH

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ABSTRACT: The intermediate band solar cell (IBSC) is a solar cell that, in order to increase its efficiency over that of single gap solar cells, takes advantage of the absorption of below-bandgap energy photons by means of an intermediate band (IB) located in the semiconductor bandgap. For this process to improve the solar cell performance, the below-bandgap photon absorption has to be effective and the IB cannot limit the open-circuit voltage of the cell. In this paper we provide a guide to the new researcher interested in the idea in order he can quickly become familiar with the concept and updated with the most relevant experimental results.
Keywords: intermediate band, quantum dots, impurities

1 INTRODUCTION

Figure 1 sketches the basic structure and fundamental operation of an intermediate band solar cell (IBSC). The electronic structure of the so-called "intermediate band material" is similar to that of a semiconductor but for the existence of a collection of energy levels (the intermediate band, IB) inside the bandgap. The IB makes possible the absorption of the below-bandgap energy photons that are wasted in conventional single gap solar cells. The photon absorption process occurs as follows: low energy photons pump electrons from the valence band (VB) to the IB (photons labeled "1" in Figure 1) and from the IB to the conduction band (photons labeled "2"). In this way, two below-bandgap energy photons create one net electron-hole pair that adds to the ones generated conventionally through transitions from the VB to the CB (photons labeled "3"). The photocurrent is then increased over that of a cell with a bandgap E_G. However, the fundamental reason why the efficiency is boosted is because the output voltage is still limited by the total bandgap and not by the presence of the IB. In this paper we provide a guide to the new researcher interested in the idea in order he can quickly become familiar with the concept and updated with the most relevant experimental results.

2 FUNDAMENTAL THEORY

The model that allows to calculate the limiting efficiency of the IBSC (63.2 % under concentrated light) appeared published in [1, 2]. In order to calculate the maximum efficiency, "photon selectivity" was assumed. Photon selectivity means that, for example, a photon like "3" in Figure 1, in spite of its high energy, cannot be absorbed through a transition demanding lower energy such as the ones from the VB to the IB. The reason why photon selectivity is needed in order to calculate the maximum efficiency is that in this way, energy losses by electron relaxation within the band are minimized [3]. It must be emphasized that this photon selectivity is needed to calculate the maximum efficiency as well as the optimum gaps leading to it. Out of these optimum bandgaps, photon selectivity might not be required to achieve the highest efficiency for the given bandgaps since losses by carrier relaxation might be compensated by a better current matching between the VB to IB and the IB to CB transition. A model to calculate the efficiency of the IBSC non assuming photon selectivity was presented in [4]. Another conceptual point to take into account is that both models presented in [1, 4] are relatively simple and, in spite of it, take into account photon recycling phenomena in the IBSCs [5]. An equivalent circuit model for the IBSC taking into account photon recycling can be found in [6, 7].

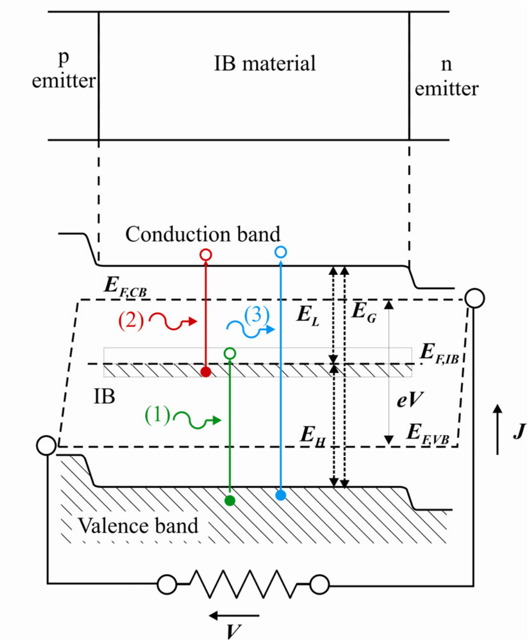

Figure 1: General structure of an IBSC and simplified bandgap diagram showing the elemental photon absorption processes that constitute the basis of its operation

The reason why it is possible to take into account photon recycling while still leading to analytical models for the IBSC is that, since these models aim to calculate the limiting efficiency, they also assume infinite mobility and therefore, constant quasi-Fermi levels. If finite mobilities and other recombination mechanisms different from the radiative one are included in the model, then, neglecting photon recycling can still lead to reasonable simple models [8] but at the price of being inaccurate when the performance of the device eventually reaches the radiative limit [9].

Usually it is demanded that the IB is partially filled with electrons so that there are empty states to receive electrons from the VB as well as electrons to be pumped from the IB to the CB. Nevertheless, it has been pointed out that under high illumination conditions such as concentrated light [10], the partial filling of the IB might be achieved by photofilling.

From a conceptual point of view, it is important to note that the process illustrated in Figure 1 is not the only one by which two below-bandgap energy photons can pump net one electron from the VB to the CB. Hence, in [11] it was described how two photons being absorbed through transitions from the VB to the IB can also generate one electron hole pair when assisted by an impact ionization process. This approach has not been attempted experimentally yet to our knowledge. This example also emphasizes that two below bandgap energy photons (and not just one) are necessary to produce the sufficient free energy to exceed the efficiency of single gap solar cells without violating the second law of thermodynamics [12].

Finally, it must be mentioned that the correct interpretation of the experimental results derived from the characterization of IBSCs requires some care since some of them, even the apparently most simple ones such as the quantum efficiency, can be counterintuitive. A recent review for the correct interpretation of experimental results related to the characterization of IBSCs can be found in [13].

3 QUANTUM DOT INTERMEDIATE BAND SOLAR CELLS

Quantum dots (QD) were proposed as one of the means to take to practice the IBSC concept [14]. Under this approach, the IB would be formed from the states of the electrons confined in the CB (Figure 2). δ–doping is often introduced to partially fill with electrons the IB. However, this δ–doping perhaps has no effect when only a few layers of QDs are grown because these layers usually are located in the space charge region of the device. In this case, the introduction of damping field semiconductor layers has been suggested as a means to take these few layers to a neutral region in the device where the δ–doping can impact the photon absorption from the IB to the CB [15].

The QD approach is, perhaps, until now, the one most experimentally researched. IBSCs based on QDs allowed experimentally demonstrating that two below-bandgap energy photons could create one electron-hole pair [16] and also obtaining an open-circuit voltage not limited by the IB [17, 18] (Figure 3). The cells were based on the InAs/GaAs QD material system. In this system, the energy of the IB is suspected to be too close to the CB so that lowering the temperature was necessary in order to inhibit electron thermal escape from the IB to the CB and achieve the aforementioned results. In order to improve these results, and approach them to room temperature operation, other material systems bases on III-Vs (such as the use of AlGaAs barriers) [19] and lead salts [20] have been proposed. The results from the characterization of the first prototypes of solar cells based InAs QD in AlGaAs barriers are consistent with the pursued enlargement of the IB to CB effective bandgap [21].

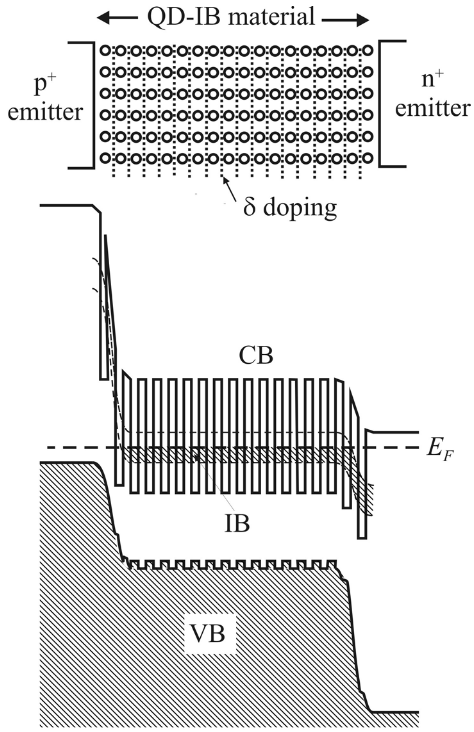

Figure 2: IBSC structure implemented with QDs and simplified bandgap diagram in equilibrium.

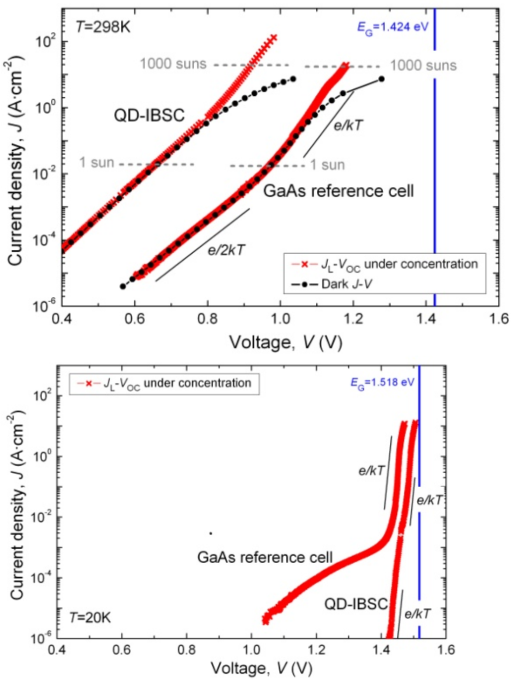

Figure 3. Short-circuit current vs open-circuit voltage of a quantum dot intermediate band solar cell implemented with InAs/GaAs QDs at (a) room temperature (b) 20 K (From [17], Copyright Elsevier, reproduced with permission).

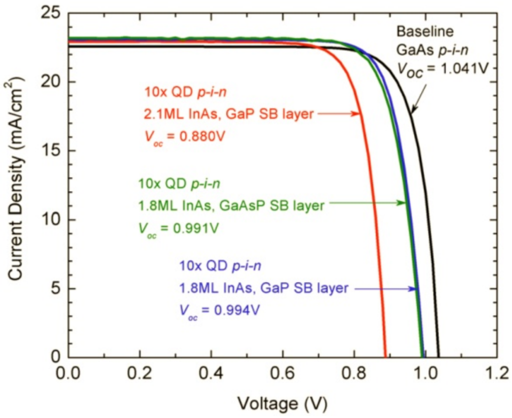

Figure 4. Current voltage characteristic of several quantum dot InAs/GaAs cell, some of them with Voc close to 1 eV. The GaAs reference cell I shown in black. (From [22]. Copyright American Institute of Physics. Reproduced with permission).

Nevertheless, still the best efficiencies have been obtained on devices based on InAs/GaAs QDs by Blokhin et al. [23] (18 %) and Bailey et al. (13.5 % with a near 1 V open-circuit voltage, Figure 4).

At present it is believed that the mean limiting factor in the performance of this kind of intermediate band solar cell is the poor photon absorption related to the IB to CB transition. Several studies have been undertaken in order to improve our understanding of this mechanism [24-26]. The possibility of implementing light management architectures, such as the insertion of metal nanoparticles [27, 28] or the use of diffracting grids [29], is also under consideration.

4 BULK INTERMEDIATE BAND SOLAR CELLS

The IB can also be created from the insertion of selected impurities into a semiconductor. In principle, when inserted at low concentrations, these impurities behave as deep centers and are detrimental to the cell performance because they introduce non-radiative recombination. However, one of the existing models supporting the formation of an IB in bulk semiconductors predicts [30] that, when inserted at sufficiently high concentrations, the wavefunction of the electrons at the impurities becomes extended and non-radiative recombination is inhibited. Experimentally, the system studied the most as a proof of concept has been perhaps the one based on the insertion of titanium into silicon. The results of experiments based in the measurement of the conductivity and mobility of the samples by Hall effect [31] as well as the lifetime of implanted wafers [32] are consistent with the formation of an IB. Encouraged by the predictions of the theory [33, 34], the insertion of some transition metals in thin films, such as Ti and Fe in $CuGaS_2$ [35, 36] has been researched experimentally. The cell with Ti showed systematically improved efficiency over their counterparts without Ti but the result is not attributed to presence of an IB but, perhaps, to a better passivation of the grain boundary. In the case of Fe it was an increase in the sub-bandgap photocurrent was observed when compared with reference cells without Fe.

Another theory framework supporting the formation of an IB is based on the band anti-crossing mechanism [37] and would explain the formation of an IB in highly mismatched alloys. This theory has been used to explain the appearance of an IB in diluted II-VI oxide semiconductors [38] and quaternary alloys [39]. Actual IBSCs have been made of ZnTe:O [40] (Figure 5), where the absorption coefficient related to the IB to CB transition in ZnTe:O has been recently measured [41], and GaNAs [42].

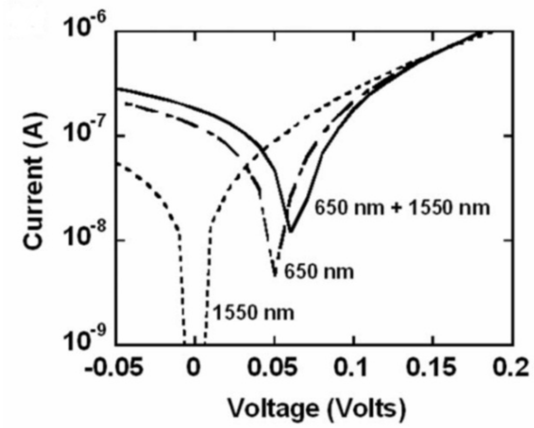

Figure 5. Current-voltage characteristic of a ZnTe:O cell when illuminated with photons that can promote electrons from the VB to the IB (650 nm), from the IB to the CB (1550 nm) and with both (650 nm+ 1550 nm). (From [40] Copyright American Institute of Physics. Reproduced with permission).

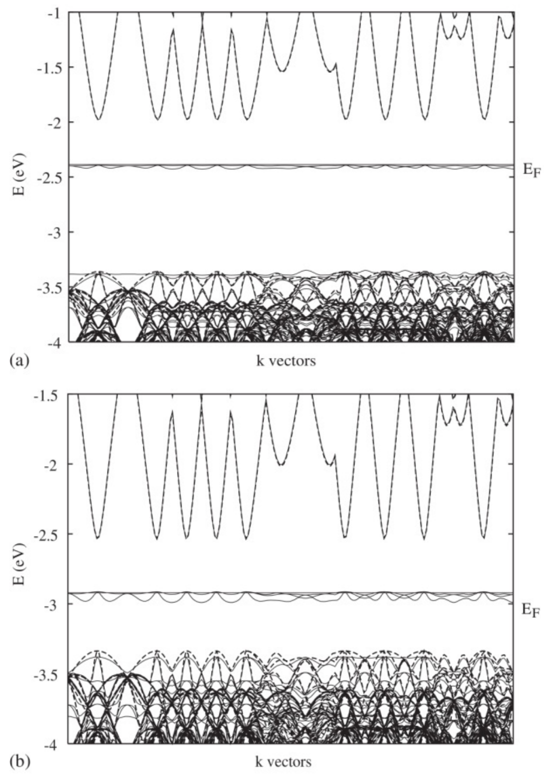

Figure 6. Example of abinitio calculations to predict intermediate band materials. The plots illustrate the energy bands (eV) in several directions of the Brillouin zone for the intermediate band materials X_{108} $Zn_{107}Cr$ for (a) X=S and (b) X=Te. (From [43], Copyright Elsevier, reproduced with permission).

5 OTHER INTERMEDIATE BAND CANDIDATES

Ab-initio calculations (Figure 6) are been carried out to predict IB materials. Profs. Wahnon, Conesa and Tablero and co-workers have, in particular, carried out and extensive work in this sense, where Refs. [44-49] are only some recent examples of their published work. Remarkably, one of these materials, V:In_2S_3, was first predicted theoretically and later synthesized [50]. The absorption spectrum of this material was consistent with the theoretical predictions. Ekins-Daukes and Schmidt [51] have proposed a molecular approach to the implementation of the intermediate band.

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